The Dimorphism and t h e Crystal Habits of Copper-Oxinate Precipitates

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8-Hydrooxyquinoline has been used in the quantitative analysis of copper. Copper-oxinate precipitates as greenish yellow needle form (α-form) at the outset and then change into a green plate form (β-form). The relation between this dimorphism and the condition of the precipitation are shown briafly in Table 1 from the results of many electron micrographs.

Table 1. Relation between the dimorphism and the condition of the precipitation.

Temperature (°C)	Conc. of $CuSO_4$ (Mole/l)	Shape of precipitate	
		at the outset	after standing
below 40°	$10^{-3}\sim20^{-2}$	needle	plat (tetra.)
	above 10^{-1}	plate (tetra.)	no change
above 40°	$10^{-3}\sim10^{-2}$	needle and plate (hex. rhom.)	slight change to plate (hex. rhom.)
	above 10^{-1}	needle and plate (hex. rhom.)	plate (hex. rhom)

From analytical results, both α- and β-form copper-oxinate precipitates had the same composition, $Cu(C_9H_6ON)_2\cdot2H_2O$.

X-ray diffraction patterns of precipitates were recorded on a diffractometer, using Ni filter copper radiation ($\lambda=1.54$ Å). It was recognized that the crystal structure differed from each other. Interplanar spacings of β-form copper-oxinate 2 hydrate had good accordance with the values calculated from the lattice constant which Kruch and Dwiggins reported. The precipitates of β-form copper-oxinate 2 hydrate are hexagonal, rhombohedral or tetragonal form, and the hexagonal form has constant plane angles at 116° and 128°. It is suggested that the flat habit surface of hexagonal plate is (100).

The X-ray pattern of α-form copper-oxinate 2 hydrate is different from that of β-form and the number of diffraction peaks is smaller than that of β-form. This fact suggests that the crystal system of unstable α-form copper-oxinate 2 hydrate belongs to the higher symmetric system such as orthorhombic, tetragonal, etc. Now, copper-phthalocyanine precipitate has also dimorphism. The space group of stable β-form copper phthalocyanine is $P_{21/a}$ as in β-form copper-oxinate 2 hydrate. It has been assumed that the α-form copper-phthalocyanine belongs to tetragonal system, by powder X-ray diffraction by Robinson et al. by electron

microdiffraction by Suito and Uyeda. The interplanar spacings of α-form copper-oxinate 2 hydrate calculated form X-ray diffraction patterns accord with the Hull and Daveys diagram for tetragonal system at the position of about 1.6 for c/a value. The interplaner spacings calculated, by assuming the cell constants as $a=b=6.57$Å, $c=15.56$Å and $\alpha=\beta=6=90°$, agreed with the above experimental results with accuracy of 1%.

It is concluded that α-form copper-oxinate 2 hydrate, which precipitates from the solution, transforms into stable β-form, in the same way as in the case of copper-phthalocyanine.

On the Leaching of Domestic Chromite Ore in Sulfuric Acid

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To obtain a pure chromic sulfate electrolyte for the production of metallic chromium, the leaching conditions of a domestic ore (48.7% Cr_2O_3 and 12.6% FeO) in sulfuric acid containing small amount of $(NH_4)_2Cr_2O_7$ were studied.

Sample : The chromite ore from Numaoshi in Hokkaido was crushed by a Engelbach crusher, and sieved by a stuandare Tyler sieve.

Operation : Crushed ore was digested in 300-ml. porcelain beaker under atmospheric presssure, or in a 2-l lean-lined autoclave under high pressure. A mixed solution of sulfuric acid and $(NH_4)_2Cr_2O_7$ was used as leaching solution. After leaching the liquor was filtered. The amounts of Fe and Cr in the filtrate and precipitate were analysed.

Items of experiments :

Table 1. Optimum leaching conditions of Numaushi chromite.

Leaching conditions	Under atomosheric press.	Under high press		
Size of ore (mesh)	−200		−200	
Conc. of H_2SO_4 (%)	70~80	60	40	20
Leaching temp. (°c)	150~170	150	170	190
Pressure (kg/cm²)	———	3	7	11
Leaching time (hr)	>2	——	>4	——
Weight ratio of H_2SO_4 to ore	6.6	——	3	——
Weight ratio $(NH_4)_2Cr_2O_7$	0.15~0.20		0.15~0.20	
Extraction of Cr(%)	90		90	